

METHOD 33

DETERMINATION OF DISSOLVED CRITICAL VOLATILE ORGANIC COMPOUNDS IN WASTEWATER SEPARATORS

REF: Reg 8-8-112
8-8-210

1) PRINCIPLE

- 1.1 This method is applicable ~~for~~ to the determination of critical volatile organic compounds (**VOC's**), as defined in Reg 8 Rule 8 Section 210 for wastewater separators.
- 1.2 The VOC's having a carbon number of C-14 or less are extracted from wastewater samples using carbon disulfide (**CS₂**), and the extract is analyzed by gas chromatography.
- 1.3 ~~It has been found that the amount of C₇ or less hydrocarbons and oxygenated compounds in these kinds of samples is insignificant, thus no attempt is made to quantitate these compounds.~~

2) APPARATUS

- 2.1 **Gas Chromatograph.** This unit is equipped ~~fitted~~ with a flame ionization detector (**FID**), a glass sleeve liquid injection port, a temperature programmer and a compatible integrator or data station.
- 2.2 **Analytical Column. (4.2.1)**
- 2.3 **Vari Whirl Mixer.**
- 2.4 **10 µl Micro Syringe.**
- 2.5 **125 ml Separatory Funnel.**
- 2.6 **50 ml ~~Graduated Cylinder~~ Volumetric Pipette.**
- 2.7 **1.0 ml Pipets.**
- 2.8 **Refrigerator.**
- 2.9 **15 ml Graduated Centrifuge Tubes, with screw caps and Teflon septa.**
- 2.10 **25 and 10 ml Volumetric Flasks.**

3) REAGENTS

3.1 Carbon disulfide, reagent grade.

3.2 Reagent grades or the best available grade of each of the following hydrocarbons; n-C₈ thru n-C₁₅. A minimum purity of 99% for each compound is acceptable.

3.3 Fuel Gas, Cylinder Hydrogen, 99.9% or higher purity. (Note 1)

3.4 Carrier Gas, Helium or Nitrogen, 99.99% or higher purity. (Note 1)

3.5 Compressed Air. (Note 1)

Note 1: The carrier and fuel gases are compressed under high pressure. Hydrogen is an extremely flammable gas. Compressed air supports combustion. Read the precautionary labels before handling these materials.

4) ANALYTICAL PROCEDURE

4.1 The samples should be processed immediately after they are received in the laboratory.

4.1.1 Shake the sample vigorously and transfer immediately to a 500 ml graduated cylinder. Let stand 10-15 minutes to allow the aqueous and hydrocarbon layers to separate. Using a 50 ml volumetric pipette, take a 50 ml aliquot portion from the aqueous layer (about 100 ml below the water-oil junction). Transfer the aliquot to a 125 ml separatory funnel.

4.1.2 Using a hood, add 10 ml of CS₂ to the sample. Invert the separatory funnel and open the stopcock to release the internal pressure.

4.1.3 Extract the hydrocarbons from the aqueous layer with careful but vigorous shaking of the mixture for a one (1) minute period. Release the built-up pressure after each shaking. Repeat the extraction step five (5) times.

4.1.4 Allow the CS₂ and aqueous layers to separate completely. Transfer the CS₂ layer (**bottom layer**) to a 15 ml centrifuge tube, cap the tube and analyze starting with (4.4.3). If analysis cannot be performed immediately, store the tube in a refrigerator. Analyze the CS₂ extract within 24 hours.

4.2 Gas Chromatograph: Column and Operating Parameters.

Column: ~~8' x 1/8" O.D. SS column packed with 10% SP-2100 in Supelco port, 100-120 mesh.~~

	<u>Initial</u>	<u>Final</u>
Oven Temperature (°C)	90	240
Time Delay (min)	0	5.0
Program Rate (°C/Min)	5	
* Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	He or N₂	
Carrier Gas Flow (cc/min)	22	
Sample Injection Size (µl)	2.0	

4.2 Gas Chromatograph (GC). (2.1) The recommended GC operating parameters are:

<u>Initial Oven Temperature (°C)</u>	<u>40</u>
<u>Initial Hold Time (min)</u>	<u>8</u>
<u>Temperature Program Rate (°C/min)</u>	<u>5</u>
<u>Final Temperature (°C)</u>	<u>200</u>
<u>Final Hold Time (min)</u>	<u>5</u>
<u>Injector Temperature</u>	<u>250</u>
<u>Detector Temperature (°C)</u>	<u>250</u>
<u>Carrier Gas</u>	<u>He</u>
<u>Carrier Gas Flow Rate (ml/min)</u>	<u>3</u>
<u>Injection Sample Size (µl)</u>	<u>1</u>

4.2.1 Analytical Column: Any analytical column capable of resolving the compounds of interest is acceptable. The recommended analytical columns for this method are:

4.2.1.1 Primary Column: 30 m x 0.32 mm DB-1 Column, 1.0 µm film thickness (J & W Scientific).

4.2.1.2 Alternate Column: 12' x 1/8" O.D. SS Column packed with 20% SP 2100 on 100/120 mesh Supelcoport. (Note 2)

Note 2: It is necessary to modify the suggested gas chromatographic parameters if the alternate column is used.

4.3 Preparation of Standard Solutions

4.3.1 Stock Hydrocarbon Standard Solution. Accurately weigh 100 mg (± 0.1 mg) of each of the following hydrocarbons in a 15 ml graduated centrifuge tube; n-C₈, n-C₉, n-C₁₀, n-C₁₁, n-C₁₂, n-C₁₃, n-C₁₄ and n-C₁₅. Thoroughly mix the solution by use of a Vari Whirl mixer. The stock standard is kept refrigerated and is stable for at least six (6) months. (NOTE 3 4)

NOTE 3 4: If the sample contains hydrocarbons lighter than n-C₈, they should be speciated and included in the standard.

4.3.2 Working Hydrocarbon Standard Solution I. Accurately weigh ~~40~~ 25 mg (± 0.1 mg) of the stock hydrocarbon standard solution in a ~~40~~ 25 ml volumetric flask and dilute to the mark with CS₂. This working standard contains ~~400~~ 125 µg of each hydrocarbon per ml. Stopper the flask, and thoroughly mix the solution by inverting the flask several times. This working standard is always prepared fresh prior to use.

4.3.3 Working Hydrocarbon Standard II. Accurately transfer 1.0 ml of (4.3.2) to 10 ml volumetric flask and dilute to the mark with CS₂. This working standard solution contains ~~40~~ 12.5 µg of each hydrocarbon per ml. Stopper the flask, and thoroughly mix the solution by inverting the flask several times. This working standard is always prepared fresh prior to use.

4.3.4 The CS₂ used for sample extractions and standard preparations must be checked for contamination. Inject 1 µl of the CS₂ into the gas chromatograph as in **Section 4.4**. Record the retention times and peak areas of the compounds, if any are present. Retain the chromatogram. (NOTE 4 2)

NOTE 4 2: CS₂ normally contains 5-10 µg/ml of benzene and approximately 1 µg/ml of thiophene. These compounds do not interfere however with the critical VOC's determination.

4.4 Analysis of Sample Extracts.

4.4.1 Set up the gas chromatograph as described in 4.2.

4.4.2 Inject ~~2~~ 1 µl of the working standard solution II (4.3.3) into the gas chromatograph using a 10 µl syringe. Record the retention times and peak areas of each compound. Retain the chromatogram.

- 4.4.3** Inject ≥ 1 μl of the CS_2 sample extract (4.1.4) into the gas chromatograph using a 10 μl micro syringe. Record the retention times and peak areas of each compound that elutes through $n\text{-C}_{15}$. Retain the chromatogram. (NOTE: 5 3).

NOTE 5 3: $n\text{-C}_{14}$ is the VOC cut off point for Reg. 8-8-210. The $n\text{-C}_{15}$ in the standard is used as a marker compound.

5) CALCULATIONS

- 5.1** Compare the chromatograms of (4.4.2) and (4.4.3) to identify the specific hydrocarbon compounds, by carbon number, in the sample. Quantitate the individual hydrocarbon compounds using the following equations.

- 5.2** **PPM = $\mu\text{g/ml}$ of an individual hydrocarbon in the sample:**

$$\text{PPM} = \frac{\text{Conc (Std) } \mu\text{g/ml} \times \text{PA (Extract)} \times 10 \text{ ml (Extract)}}{\text{PA (Std)} \times 50 \text{ ml (Sample)}}$$

Where: **PA (Extract)** = Peak Area of the individual hydrocarbon found in the CS_2 sample extract (4.4.3)

Conc, (Std) = Concentration in $\mu\text{g/ml}$ of each corresponding hydrocarbon in the working standard (4.3.3).

10 = Volume of CS_2 in ml, used in the sample extraction.

PA (Std) = Peak Area of the corresponding hydrocarbon in the standard solution (4.3.3).

50 = Volume in ml of the sample (4.1.1).

- 5.3** Total PPM ($\mu\text{g/ml}$) of C_{14} and less hydrocarbon in the wastewater separator is equal to the sum of each compound found and quantified in (5.2).

6) REFERENCES

- 6.1** Control Techniques for VOC Emissions from Stationary Sources, EPA 450/7-78-023, May 1978.
- 6.2** Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, ASTM D 2887-84, 1986 Annual Book of ASTM methods, Section 5.